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Mineral Concentrations of Forage Legumes and Grasses Grown in Acidic Soil Amended with Flue Gas Desulfurization Products

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ABSTRACT

Considerable quantities of flue gas desulfurization products (FGDs) are generated when coal is burned for production of electricity, and these products have the potential to be reused rather than discarded. Use of FGDs as soil amendments could be important in overall management of these products, especially on acidic soils. Glasshouse studies were conducted to determine shoot concentrations of calcium (Ca), sulfur (S), potassium (K), magnesium (Mg), phosphorus (P), boron (B), zinc (Zn), copper (Cu), manganese (Mn), iron (Fe), aluminum (Al), sodium (Na), molybdenum (Mo), nickel (Ni), cadmium (Cd), chromium (Cr), and lead (Pb) in alfalfa (*Medicago sativa*), white clover (*Trifolium repens*), orchardgrass (*Dactylis glomerata*), tall fescue (*Festuca arundinacea*),

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switchgrass (*Panicum virgatum*), and eastern gamagrass (*Tripsacum dactyloides*) grown in acidic (pH 4) soil (Typic Hapludult) amended with various levels of three FGDs and the control compounds CaCO_3 , CaSO_3 , and CaSO_4 . Shoot concentrations of Ca, S, Mg, and B generally increased as levels of soil applied FGD increased. Concentrations of Mn, Fe, Zn, Cu were lower in shoots, especially when soil pH was high (>7). Shoot concentrations of the trace elements Mo, Ni, Cd, Cr, and Pb were not above those reported as normal for foliage. Overall concentrations of most minerals remained near normal for shoots when plants were grown in FGD amended acidic soil.

Key Words: Macro nutrients; Micro nutrients; Non essential trace metals; Flue gas desulfurization products; Legumes; Grasses; Acid soil.

INTRODUCTION

Use of desulfurization products (FGDs) as a soil amendment could be important in overcoming the overall management of these coal combustion byproducts. As a soil amendment, FGDs could increase pH of acidic soils for alleviation of mineral toxicities/deficiencies, provide some mineral nutrients to plants, improve soil physical properties (increase water infiltration, soil water holding capacity, and soil aggregation, and decrease soil crusting and erosion), reduce P run-off from high-P surface soils to decrease stream/estuary contamination, and enhance co-utilization with organic wastes/manures.^[1–12]

The composition of FGDs varies extensively depending on many factors such as power plant systems (e.g., scrubbing technology, boiler type, type of coal, burning conditions, “forced oxidation”), type of limestone (Ca sorbent) used to “scrub” S from gas streams, and supplemental materials added to end-products. Many systems produce slurries composed primarily of CaSO_3 that need to be stabilized by adding other materials like fly and bottom ashes, calcined lime [CaO , $\text{Ca}(\text{OH})_2$], and/or additional limestone. CaSO_3 may also be oxidized to CaSO_4 (FGD gypsum) (CaSO_4 is used throughout the text for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$). FGDs contain especially high concentrations of Ca and S and may also contain other mineral elements essential to plant growth (e.g., Mg, B, Zn, Cu, and Mo), and some essential plant growth minerals at levels that may become toxic to plants (e.g., Zn, Cu, Mo, Ni, and Se). The added substances like fly and bottom ashes to FGDs may contain high concentrations of B and some undesirable/toxic trace mineral elements

(e.g., As, Cd, Cr, and Pb). If dolomitic limestone is added, enhanced amounts of Mg would also be included in FGDs.

If FGDs are used as soil amendments, information about their effects on plant acquisition of mineral nutrients is needed. Shoot concentrations of Ca, S, B, Mg, and Mn were high (excessive in many cases) when maize (*Zea mays* L.) was grown in acidic soil amended with high levels of certain FGDs, but most mineral elements essential to plant growth were present at near normal concentrations.^[13] Decreases in shoot concentrations of many mineral elements occurred when soil pH was high (≥ 7) as a result of added FGDs. In these studies, levels added were from 5 to 10% (to convert percentage values in soil mixes to metric ton ha^{-1} multiply by 22) for non-stabilized and stabilized FGDs and up to 75% for FGD gypsums. Symptoms of Al toxicity and P and Mg deficiencies frequently appeared when maize was grown in unamended acidic soil in other studies.^[14–17] and many of these symptoms were commonly overcome as levels of some FGDs increased.^[13] Boron toxicity symptoms appeared in maize grown at the highest levels of some FGDs,^[18] while trace element concentrations were not above those reported as normal for plant tissue.^[19]

A FGD gypsum product increased S concentrations in coastal bermudagrass [*Cynodon dactylon* (L.) Pers.] foliage when plants were grown with 0.25 and 0.5 metric ton ha^{-1} applications to soil over two years.^[20] The initial soil S was low (25 mg kg^{-1} soil) and FGD application increased soil S concentrations. Foliar S concentration at the highest level of FGD added (4.1 g kg^{-1}) approached that considered potentially harmful to animals,^[21] while the other mineral elements were normal for plant tissue. Alfalfa (*Medicago sativa* L.) grown over two years in acidic soil amended with a FGD gypsum product had increased S concentrations when FGD was added was at the highest level (18 metric ton ha^{-1}).^[22] Sulfur accumulated to concentrations (4.0 g kg^{-1}) that approached toxic limits for animals.^[21] However, trace element concentrations were below USEPA 503 standards.^[23] Citrus (*Citrus* spp.) grown in sandy soil with low extractable Ca had increased Ca acquisition when FGD gypsum was applied at 2.24, but not 1.12, metric ton ha^{-1} .^[24] The enhanced Ca was not antagonistic to Mg and K acquisition. Only concentrations of B, As, and Se were above normal when maize was grown with 8 and 10% FGD in soil, while other mineral elements remained fairly normal at these same levels of added FGD.^[25]

Enhanced tissue concentrations of Ca, S, Mg, B, and Mo were noted for alfalfa and tall fescue (*Festuca arundinacea* Schreber) grown in acidic (pH 4.6) soil amended with dry FGD products [fluidized bed combustion product (FBC)], and alfalfa had higher concentrations than tall fescue.^[26] Tissue from field grown alfalfa had increased S, Mg, B, and Mo and decreased Mn, Zn, and

Ni concentrations the second year after surface application of various levels of a dry FBC + Mg product.^[27] In both of these studies, concentrations of most mineral elements in tissue did not change significantly when plants were grown in amended soil. However, the highest level of FBC added was only 2-fold higher than the lime requirement for soil, which meant that relatively low levels (e.g., ~1.0–1.5% in soil) were added.

The objective of our study was to determine shoot concentrations of mineral elements in six forage species grown in acidic soil unamended and amended with different levels of three FGDs. Plants were also grown in acidic soil amended with different levels of the control compounds CaCO_3 , CaSO_3 , and CaSO_4 for comparison with FGDs.

MATERIALS AND METHODS

Only limited information about procedures and growth conditions has been described here, since a companion article provides more detail.^[28] Properties of the acidic soil and FGDs used are listed in Tables 1 and 2. FGD-22 was a FGD gypsum product, FGD-27 was a FGD-gypsum + Mg [6% $\text{Mg}(\text{OH})_2$] product, and FGD-28 was a stabilized CaSO_3 FGD product. The control compounds were chemical grade CaCO_3 , CaSO_3 , and CaSO_4 .

Soil was thoroughly mixed with fertilizer (50 N as NH_4NO_3 and 143 P as KH_2PO_4 in mg kg^{-1} soil) and FGD/control substances at various levels, wet to

Table 1. Properties of acidic Lily soil before addition of amendments.

Property/element	Unit	Value	Element	Unit	Value
<i>Fine loamy, siliceous, mesic, Typic Hapludult</i>					
Sand	%	43.1	1 M NH_4 -acetate extractable ions		
Silt	%	38.8	Ca	mg kg^{-1}	45.8
Clay	%	18.2	K	mg kg^{-1}	69.5
Organic matter	%	4.70	Mg	mg kg^{-1}	5.06
pH _W (1 soil:1 water)		4.48	Na	mg kg^{-1}	2.30
pH _{Ca} (1 soil:1 10 mM CaCl_2)		3.89	S	mg kg^{-1}	70.0
EC (1 soil:1 water)	dS m^{-1}	0.06	5 mM DTPA extractable ions		
Cation exchange capacity	$\text{cmol}_c \text{ kg}^{-1}$	3.82	Mn	mg kg^{-1}	33.1
Al (1 M KCl extractable)	$\text{cmol}_c \text{ kg}^{-1}$	3.36	Fe	mg kg^{-1}	53.8
Al saturation	%	88.0	Zn	mg kg^{-1}	0.716
P (Bray-1 extractable)	mg kg^{-1}	3.09	Cu	mg kg^{-1}	0.125

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Table 2. Some properties of FGDs used to amend acidic soil.^a

Property	Unit	FGD-22	FGD-27	FGD-28
pH (1 FGD:1 water)		8.91	9.53	8.68
pH (1 FGD:2 water)		8.96	9.65	8.82
EC (1 FGD:1 water)	dS m ⁻¹	1.67	3.35	5.58
EC (1 FGD:2 water)	dS m ⁻¹	1.92	3.29	4.17
CCE ^b	%	5.0	13.1	69.3
Chemical element				
S-SO ₃	g kg ⁻¹	0.8	1.0	25.9
S-SO ₄	g kg ⁻¹	216	176	200
Ca	g kg ⁻¹	238	209	509
Mg	g kg ⁻¹	0.23	22.7	24.4
K	mg kg ⁻¹	32	165	88
P	mg kg ⁻¹	60.7	<0.03	90.7
B	mg kg ⁻¹	<0.02	99.0	7.81
Mn	mg kg ⁻¹	58.4	85.5	101
Fe	mg kg ⁻¹	441	1050	1330
Zn	mg kg ⁻¹	<0.01	2.52	189
Cu	mg kg ⁻¹	<0.01	0.12	1.18
Al	mg kg ⁻¹	37	1220	690
Na	mg kg ⁻¹	483	424	274
Mo	mg kg ⁻¹	1.61	0.63	2.00
Ni	mg kg ⁻¹	2.11	6.10	60.9
Cd	mg kg ⁻¹	0.14	<0.01	68.8
Cr	mg kg ⁻¹	86.0	74.2	15.0
Pb	mg kg ⁻¹	17.1	10.8	<0.1

^a Additional properties of FGD-22(BP-#22) and FGD-27 (BP-#27) are reported in Clark et al.^[14]^b CCE = Calcium carbonate equivalency.

field capacity with distilled water, equilibrated seven days, and placed in plastic pots (1.0 kg soil mix pot⁻¹). See data tables for levels of each FGD/control compound added. Plant species grown in the experiments were: two legumes [alfalfa (*Medicago sativa* L. cv. 'Vernal') and white clover (*Trifolium repens* L. cv. 'Huia')], two cool-season grasses [orchardgrass (*Dactylis glomerata* L. cv. 'Wana') and tall fescue (*Festuca arundinacea* Schreber cv. 'KY31')], and two warm-season grasses [switchgrass (*Panicum virgatum* L. cv. 'Cave-in-Rock') and eastern gamagrass (*Tripsacum dactyloides* L. cv. 'WW1459')]. Each forage species was grown in unamended acidic soil and in soil treated with each FGD and control compound in each experiment (three plants pot⁻¹), and each species was included in at least two



experiments (except alfalfa which was included in only one experiment). Because of the large number of treatments and plant species, experiments were conducted over time. Deionized water was added manually as needed to avoid splashing on stalks and leaves and to provide sufficient water for growth. Care was taken to avoid leaching from pots. Plants were grown in a glasshouse for 82 d (alfalfa), 59 d (white clover), 55 d (orchardgrass), 54 d (tall fescue), 69 d (switchgrass), and 71 d (eastern gamagrass).

At harvest, shoots were severed ~1 cm above the soil surface or ~0.5 cm above the crown, dried, weighed, and ground to pass a 2 mm screen. Samples of ground shoot material were weighed (50–100 mg) into a Teflon container, digestion solution (1.0 mL 15.8 M HNO₃) was added, and containers were placed in microwave digestion bombs (Parr Instrument Co., Moline, IL^a). These samples were microwaved 4 min at 70% power followed by 2 min at full power (635 W), allowed to cool in the microwave 5 min, and removed to cool at ambient temperature. Digested solutions were brought to a final volume of 10.0 mL with distilled deionized water. Solutions were filtered and analyzed for mineral elements by inductively coupled plasma spectroscopy (JY46P model, Jobin Yvon Emission, Longjumeau, France^a). If digested samples had to be stored before analysis, they were filtered, placed in plastic containers, and stored at –10°C.

The experimental design was a completely randomized block with four replications, except the alfalfa experiment, which had six replications. Least significance differences (LSD) at $P < 0.05$ were used to evaluate differences among means.^[29]

RESULTS AND DISCUSSION

Information about FGD effects on soil pH and EC and plant growth traits is the subject of a companion article^[28]; hence the current article addresses only mineral acquisition by the same plants.

Macronutrients

Plants grown in unamended soil had low shoot Ca, and Mg concentrations (near or below concentrations considered deficient), while S and K

^aMention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture.



concentrations were normal (Tables 3–5). Although differences were small for plants grown in unamended soil, the legumes had highest shoot Ca concentrations and the warm-season grasses had lowest (Table 3). With few exceptions, similar patterns with larger differences were noted when plants were grown at the various levels of control compounds and FGDs. Except for plants grown with CaSO_3 , shoot concentrations of Ca generally increased as level of control compound and FGD increased in soil. A major exception was the decreased Ca concentrations in the legumes grown with increased levels of FGD-27. This decrease in Ca probably occurred because FGD-27 contained relatively high Mg (Table 2), and Mg and Ca interact with each other.^[16,32,33] Addition of FGD-27 also increased soil pH extensively,^[28] and high soil pH ($>7-8$) often induces other disorders (e.g., P, Zn, and Fe deficiencies) in plants.^[34] Highest shoot Ca concentrations were noted in plants grown with CaSO_4 and FGD-22, which were added to soil at levels up to 75%. In some cases, Ca concentrations could be considered sufficiently high to potentially induce detrimental effects on plants, mainly through exclusion of Mg (Table 3). Plants with highest Ca concentrations had relatively low Mg concentrations (Table 4).

Shoot S concentrations for each species grown in unamended soil were similar, and alfalfa generally had high or the highest S concentrations across all levels of FGD/control compounds added to soil (Table 3). Highest S concentrations in alfalfa were for plants grown with CaSO_3 . Plants that did not grow well with added CaSO_3 , which included alfalfa, had high shoot S concentrations. These high S concentrations could have been near or above those considered high for animal consumption.^[21] These high S concentrations may have occurred because of rupture of root membranes allowing S to pass freely into roots. In addition, S as SO_3 , can be highly detrimental to growth of many plants.^[13,15,28,35,36] As expected, shoot S concentrations for plants grown with different levels of CaCO_3 were similar, since CaCO_3 did not contain S (Table 3). However, S concentration increased in plants grown with increased levels of the S-containing FGDs, CaSO_3 , and CaSO_4 . Warm-season grasses usually had lower S concentrations than cool-season grasses and legumes.

Shoot K concentrations were similar in each species over treatment levels of amendments, including plants grown in unamended soil, and concentrations were mostly within normal ranges reported for plants (Table 4). Shoot Mg concentrations in plants grown in unamended soil were at or below those considered deficient (Table 4). Except for orchardgrass, Mg concentrations were considerably higher when plants were grown with CaCO_3 compared to unamended soil. Raising soil pH with CaCO_3 may have made Mg more available to plants, as noted for maize.^[16] Plants grown in soil with added



Table 3. Shoot Ca and S concentrations of six forage species grown in acidic soil amended with various levels of CaCO_3 , CaSO_3 , CaSO_4 , and three FGDs.^a

Treatment	Level in soil %	Calcium concentration (g kg^{-1} DM)						Sulfur concentration (g kg^{-1} DM)					
		ALF	WC	ORG	TF	SWG	EGG	ALF	WC	ORG	TF	SWG	EGG
Control	0	2.7	3.3	1.40	2.07	0.76	0.95	3.64	2.89	4.68	3.20	2.34	2.24
CaCO_3	0.125	18.8	14.6	4.60	3.12	1.94	2.39	3.63	2.14	4.55	3.48	1.91	2.01
	0.25	25.1	18.0	6.43	3.57	2.27	2.57	3.34	2.32	3.51	3.34	1.52	1.94
	0.5	31.7	16.7	9.42	4.11	2.91	3.45	3.40	2.54	3.92	4.21	1.65	2.02
CaSO_3	0.25	10.4	2.7	4.09	11.34	0.91	1.64	12.84	7.10	6.68	8.42	2.44	3.06
	0.5	13.1	2.9	5.34	13.24	0.76	1.65	22.18	8.95	6.87	10.20	3.27	3.06
	1.0	2.5	D	4.93	5.36	0.92	1.74	36.55	D	4.56	5.20	4.20	3.54
	2.0	D	D	6.32	4.71	1.09	D	D	D	4.48	4.90	6.96	D
	3.0	D	D	6.25	5.18	0.19	D	D	D	3.74	4.48	6.81	D
CaSO_4	5	23.9	11.0	5.13	6.25	2.52	1.18	10.79	6.29	5.48	6.18	1.87	8.50
	10	29.6	8.7	8.94	7.73	2.94	2.30	10.77	7.42	6.77	8.04	1.99	10.86
	25	31.5	12.1	5.79	8.19	2.67	6.15	8.23	6.52	5.81	7.10	1.90	5.15
	50	19.8	17.7	29.73	18.04	2.65	4.10	8.21	7.55	23.40	14.26	1.82	3.52
	75	24.4	17.3	38.90	23.08	2.52	3.84	10.09	9.52	24.18	17.78	1.90	4.01
FGD-22	5	31.4	23.1	5.93	4.99	3.27	5.38	5.46	3.89	4.18	4.76	1.60	3.40
	10	38.1	22.1	6.83	6.31	3.04	3.73	4.54	3.60	4.26	4.85	1.42	2.10



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FGD-27	25	39.6	22.3	11.42	8.04	3.04	4.30	4.22	4.57	6.16	3.96	1.08	1.96
	50	39.4	24.6	11.75	14.17	7.47	4.81	4.84	5.72	4.10	6.41	1.96	1.80
	75	36.1	24.6	14.17	17.45	8.00	4.85	4.88	7.23	4.51	6.14	2.08	1.85
	1.0	24.3	20.3	4.55	3.23	2.74	2.56	5.60	3.52	3.25	3.00	1.91	1.94
	2.5	22.2	20.1	4.19	3.95	1.64	2.45	5.90	4.07	3.10	2.90	1.92	2.20
	5.0	16.3	14.4	3.15	3.20	1.70	1.94	5.92	4.89	3.06	2.87	2.15	2.12
FGD-28	10	15.1	13.0	3.83	2.88	1.56	1.79	5.43	5.30	2.95	2.36	2.82	2.16
	25	14.1	18.1	3.49	3.96	2.52	2.60	7.11	7.46	3.10	2.76	2.33	3.08
	0.25	18.7	12.4	3.91	2.97	1.94	2.30	9.15	3.18	3.61	4.55	2.27	2.23
	0.5	20.9	19.0	5.15	3.76	2.33	2.50	9.35	3.91	4.61	4.39	2.60	2.16
	1.0	28.0	22.1	4.44	4.51	2.39	2.90	10.15	3.75	3.54	4.64	2.80	2.14
	2.0	26.0	27.8	4.45	3.22	2.35	2.92	8.10	4.20	3.19	2.82	3.02	1.97
LSD (P < 0.05)	3.0	22.3	26.1	5.19	4.73	2.22	3.36	9.03	4.20	3.21	3.56	3.20	2.35
Defic. conc. ^b		1.0	0.6	1.13	0.92	0.28	0.67	0.49	0.29	0.31	0.74	0.23	0.38
High conc. ^b		1–2.5	3–5	5	2–3 ^c	1	2–3 ^c	1.5–2	1.5–2	1.2	1–2 ^c	1–2 ^c	1–2 ^c
		30	10	10	10 ^c	10 ^c	10 ^c	5	5	2.5	4 ^c	4 ^c	4 ^c

D = dead plants.

^a Plant species were alfalfa (ALF), white clover (WC), orchardgrass (ORG), tall fescue (TF), switchgrass (SWG), eastern gamagrass (EGG).^b Deficiency (defic.) and high/toxic concentrations (conc.) were taken from Smith^[30] and Jones et al.^[31]^c Values are for an assortment of forage grasses.



Table 4. Shoot K and Mg concentrations of six forage species grown in acidic soil amended with various levels of CaCO₃, CaSO₃, CaSO₄, and three FGDs.^a

Treatment	Level in soil %	Potassium concentration (g kg ⁻¹ DM)						Magnesium concentration (g kg ⁻¹ DM)					
		ALF	WC	ORG	TF	SWG	EGG	ALF	WC	ORG	TF	SWG	EGG
Control	0	23.5	31.2	33.3	33.2	29.1	18.9	1.07	0.96	0.31	0.14	0.50	0.13
CaCO ₃	0.125	32.3	22.3	29.8	22.5	21.2	17.5	6.94	4.88	0.24	2.11	2.33	0.52
	0.25	28.3	22.2	26.2	23.1	18.1	16.5	5.56	4.92	0.42	3.12	2.36	0.60
CaSO ₃	0.5	23.0	19.0	30.8	21.6	17.7	13.2	5.69	4.82	0.43	4.09	2.80	0.60
	0.25	31.4	18.0	32.7	33.6	29.7	21.4	1.22	0.99	0.39	0.06	0.64	0.14
	0.5	24.1	13.3	32.0	33.1	26.6	19.2	1.12	0.38	0.42	0.26	0.67	0.17
	1.0	11.7	D	28.3	34.3	21.4	20.1	0.70	D	0.33	0.29	0.61	0.14
	2.0	D	D	24.7	28.9	12.2	D	D	D	0.43	0.34	0.55	D
CaSO ₄	3.0	D	D	22.1	25.3	19.9	D	D	D	0.67	0.74	0.50	D
	5	27.8	27.8	33.4	34.3	21.9	0.2	1.24	0.27	0.36	0.05	0.44	0.01
	10	37.0	29.6	31.4	32.9	22.8	0.3	1.58	0.22	0.24	0.01	0.46	0.01
	25	37.1	31.6	29.8	32.1	22.6	0.2	1.19	0.51	0.25	0.01	0.40	0.08
	50	44.5	29.7	24.8	26.4	23.1	0.2	1.66	0.54	0.24	0.01	0.37	0.12
FGD-22	75	36.4	31.6	28.3	31.7	24.0	—	0.99	0.72	0.26	0.22	0.31	0.24
	5	33.3	32.2	21.0	24.6	19.1	20.9	2.25	2.37	0.49	0.54	0.66	0.34
	10	25.6	26.5	18.9	22.4	18.7	16.7	2.24	2.51	0.99	1.37	1.02	0.24



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FGD-27	25	25.5	24.3	17.3	22.6	14.8	14.9	2.12	2.64	1.58	2.65	1.33	0.22
	50	26.8	27.6	26.6	23.8	26.9	15.5	2.33	3.02	1.48	3.08	2.91	0.34
	75	27.9	24.0	29.0	26.8	30.8	17.5	2.79	3.11	1.38	2.95	3.62	0.39
	1.0	26.7	33.0	23.0	23.6	17.9	16.6	6.18	9.87	2.79	4.14	3.20	0.76
	2.5	23.0	23.3	22.0	22.0	18.3	18.6	5.24	12.71	3.76	3.12	3.78	1.46
	5.0	22.5	21.9	21.8	15.8	19.2	17.8	2.99	10.64	3.89	4.20	4.33	1.89
	10	22.4	23.2	24.6	22.1	19.9	16.3	2.57	12.15	5.18	4.94	5.47	2.72
FGD-28	25	17.6	25.4	28.7	26.4	5.9	11.1	3.48	17.87	5.34	5.12	6.46	6.38
	0.25	43.6	33.3	22.3	27.4	25.5	19.9	3.20	3.16	0.66	0.39	1.22	0.20
	0.5	37.5	36.3	24.7	23.4	20.4	18.3	3.77	4.67	1.26	0.87	1.51	0.23
	1.0	34.9	36.1	21.9	23.6	23.1	17.8	5.01	6.61	1.31	1.67	1.76	0.31
	2.0	32.9	36.0	22.0	21.3	20.1	17.3	5.50	9.96	2.43	2.32	2.52	0.46
	3.0	27.9	31.4	23.2	24.1	18.2	18.3	5.35	11.52	3.04	3.40	3.20	0.93
LSD ($P < 0.05$)		1.3	0.67	0.71	1.0	1.5	0.8	0.15	0.22	0.05	0.06	0.20	0.10
Defic. conc. ^b		15	8–10	20	25	5–10	15 ^c	1–2	1.5–2	1.5	1–2 ^c	1–2 ^c	1–2 ^c
High conc. ^b		35	25	35	40	30 ^c	30	10	3	3	5 ^c	5 ^c	5 ^c

D = dead plants.

^a Plant species were alfalfa (ALF), white clover (WC), orchardgrass (ORG), tall fescue (TF), switchgrass (SWG), eastern gamagrass (EGG).^b Deficiency (defic.) and high concentrations (conc.) were taken from Smith^[30] and Jones et al.^[31]^c Values are for an assortment of forage grasses.

Table 5. Shoot P and B concentrations of six forage species grown in acidic soil amended with various levels of CaCO₃, CaSO₃, CaSO₄, and three FGDs.^a

Treatment	Level in soil %	Phosphorus concentration (g kg ⁻¹ DM)						Boron concentration (mg kg ⁻¹ DM)					
		ALF	WC	ORG	TF	SWG	EGG	ALF	WC	ORG	TF	SWG	EGG
Control	0	1.72	1.59	3.58	2.75	2.12	0.99	18	41	32	114	10	16
CaCO ₃	0.125	2.63	1.47	3.86	1.34	1.85	0.81	57	22	17	14	11	14
	0.25	1.74	1.66	2.62	1.61	1.43	0.73	52	26	14	16	9	14
	0.5	1.65	2.14	4.19	1.81	1.44	1.07	55	25	16	13	11	17
CaSO ₃	0.25	1.12	1.43	3.98	2.89	2.17	1.31	46	50	25	72	9	19
	0.5	1.14	1.44	3.30	3.03	2.48	1.44	51	51	24	77	16	19
	1.0	1.02	D	3.74	3.93	2.30	1.65	37	D	20	74	14	21
CaSO ₄	2.0	D	D	2.57	2.64	1.98	D	D	D	13	22	5	D
	3.0	D	D	1.94	2.27	1.68	D	D	D	9	17	11	D
	5	1.56	1.00	2.33	1.92	1.49	1.36	41	58	44	56	9	86
	10	1.27	1.14	2.26	2.67	1.61	1.79	48	41	44	49	15	63
	25	1.41	2.50	3.27	2.56	1.51	2.58	36	29	22	111	9	49
FGD-22	50	2.36	1.50	3.15	3.06	2.00	1.98	26	31	—	93	11	31
	75	3.43	4.12	5.84	4.98	2.62	2.48	21	24	27	56	9	18
	5	1.97	1.56	2.18	1.98	1.28	1.39	99	42	22	34	14	28
	10	1.54	1.49	2.20	2.32	1.26	0.90	129	54	34	51	19	32



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FGD-27	25	1.67	1.74	3.41	2.76	1.11	0.75	170	54	59	75	19	47
	50	2.25	2.13	7.39	4.45	3.08	0.63	185	85	155	180	43	77
	75	2.62	1.93	8.79	9.10	5.03	0.77	231	128	199	232	144	163
	1.0	1.92	1.31	2.17	3.29	1.35	0.86	176	66	72	203	58	101
	2.5	1.90	1.49	2.67	1.77	1.56	0.97	264	105	155	86	124	348
	5.0	1.77	1.50	3.89	2.68	1.81	0.98	269	131	198	174	205	412
FGD-28	10	1.88	1.65	3.59	2.96	2.52	0.80	285	140	258	225	356	513
	25	1.98	1.08	3.63	3.51	0.75	0.89	277	201	338	266	421	613
	0.25	1.62	1.53	1.71	1.92	1.82	0.97	91	47	17	24	14	17
	0.5	2.16	1.17	1.68	1.62	1.56	0.83	122	41	25	30	17	25
	1.0	2.07	1.25	1.94	1.94	1.50	0.82	139	41	27	45	18	34
	2.0	2.55	1.11	2.96	2.41	1.77	0.79	196	59	77	76	54	71
LSD (P < 0.05)	3.0	2.53	1.33	3.80	3.81	2.17	0.92	221	95	143	145	120	146
		0.11	0.09	0.15	0.19	0.21	0.17	5	3	3	5	12	27
Defic. conc. ^b		2	2–3	2	2	0.5	1.5 ^c	20	20	8	3–5	3–5 ^c	3–5 ^c
High toxic conc. ^b		7	4	3.5	2.5	4 ^c	4 ^c	100	50	20	25 ^c	25 ^c	25 ^c

D = dead plants.

^a Plant species were alfalfa (ALF), white clover (WC), orchardgrass (ORG), tall fescue (TF), switchgrass (SWG), eastern gamagrass (EGG).^b Deficiency (defic.) and high/toxic concentrations (conc.) were taken from Smith^[30] and Jones et al.^[31]^c Values are for an assortment of forage grasses.

CaSO_3 and CaSO_4 had markedly lower Mg concentrations than plants grown in soil with added FGDs. Increased shoot Mg in plants grown with FGD-27 and FGD-28 might be expected since these FGDs contained considerable Mg (Table 2), but CaSO_3 and CaSO_4 were chemical grade and should not have contained Mg. The accentuation of Ca:Mg imbalances from added Ca in CaSO_3 and CaSO_4 , which had no supplemental Mg, could potentially induce Mg deficiency. Magnesium deficiency is common for many plants grown in acidic soil,^[37,38] and was observed in many of our earlier studies where plants were grown in acidic soil.^[14–17] Ratios of Ca:Mg in soil should be $\sim 30\text{--}50:1$ to alleviate Mg deficiency in maize.^[16] Grasses with low Mg may also induce hypomagnesium (“grass tetany”) in grazing animals.^[39] Some of the best plant growth in our study occurred when plants were grown with low levels of FGD-27, which contained Mg,^[28] and the best growth of maize occurred when plants were grown with FGD-27 at low levels.^[14]

Shoot P concentrations were relatively low in plants grown in unamended soil, and the legumes and warm-season grasses had P at or near deficiency concentrations (Table 5). Overall, both cool-season grasses generally had higher P than the legumes and warm-season grasses for plants grown with the various treatments. The soil used in our study contained relatively low P (Table 1). The low shoot P concentrations in the legumes and warm-season grasses occurred even though some P was added to the soil before plants were grown (143 mg kg^{-1} soil). Plants grown with added CaSO_4 , FGD-22, and FGD-28 did have improved P concentrations compared to those grown in unamended soil. Both FGD-22 and FGD-28 contained considerable P, while FGD-27 did not (Table 2). Eastern gamagrass consistently had low shoot P concentration compared to the other forage species. Since hydrous oxides of Al and Fe in soil retain considerable amounts of added P, P added to soil commonly precipitates as Ca, Fe, and Al phosphates and/or is inactivated by these cationic elements forming chemical bonds at surfaces of soil minerals.^[40,41] Both Al and Fe are relatively high in Lily soil (Table 1), and this soil has potential to fix relatively high amounts of P.^[42] Anghinoni et al.^[42] also reported that the amount of P adsorbed on Lily soil was related to Fe oxide content.

Micronutrients

Shoot B concentrations were normal for plants grown in unamended soil and with varied levels of CaCO_3 , CaSO_3 , and CaSO_4 , but consistently increased in these with the FGDs (Table 5). Plants had highest B concentrations when grown with FGD-27, which contained the highest B

level of the FGDs (Table 2). Leaf B concentrations considered to be high have been reported as 25–50 mg kg⁻¹ dry matter in grasses and 50–100 mg kg⁻¹ in legumes (Table 5). However, B concentrations may be higher than this before growth diminishes. For example, maize had ~200 mg B kg⁻¹ before growth decreased,^[18] even though B has been reported to be excess to toxic at >50–100 mg kg⁻¹ in tissue.^[30,31] Many plants tolerate B concentrations up to or near 200 mg B kg⁻¹ dry matter.^[43] Plants with B at concentrations that might be considered toxic or detrimental to growth were noted for those grown with added FGD-27 at the highest levels (Table 5). Unlike the other forage species included in our study and many other plants, alfalfa is known to require high concentrations of B.^[43]

Among the highest shoot Zn and Cu concentrations noted were for plants grown in unamended soil and with added CaSO₃ and CaSO₄ (Table 6). Plants grown with CaCO₃ and FGD-27 consistently had reduced Zn and Cu concentrations as level of material added to soil increased. Addition of CaCO₃ and FGD-27 increased soil pH to 4.46 to 5.44 and 4.33 to 7.85, respectively.^[28] Such increases in soil pH could have restricted the accumulation of these mineral elements in plant tissue. Soil availability and plant acquisition of Zn and Cu normally decrease as soil pH increases.^[44] In the current study, shoot concentrations of both Zn and Cu were on the high side and could possibly have been detrimental to growth. However, growth reductions did not appear to be related to the high shoot Zn and Cu concentrations as reported earlier.^[28] No plants contained deficient concentrations of Zn and Cu, nor did they exhibit deficiency symptoms.

Plants growth in unamended soil and with added CaSO₃, CaSO₄, and FGD-28 had overall highest Mn and Fe concentrations in shoots compared to plants grown with the other amendments (Table 7). The legumes consistently had higher Mn and often higher Fe concentrations than the grasses. Manganese and Fe concentrations were reduced as soil pH increased likely because of reduced soil availability with increased soil pH.^[44] Like Zn and Cu, Mn and Fe concentrations were on the high side and may have been detrimental to plant growth. Again, growth did not appear to be related to these relatively high concentrations of Mn and Fe.^[28]

Non-essential and Trace Minerals

Shoot concentrations of Al and Na were high in plants grown in unamended soil and in soil amended with CaSO₃ and CaSO₄ (Table 8). Plants with highly restricted growth, such as those grown with CaSO₃, had especially high Na. It was assumed that CaSO₃ likely damaged root cell membranes to

Table 6. Shoot Zn and Cu concentrations of six forage species grown in acidic soil amended with various levels of CaCO_3 , CaSO_3 , CaSO_4 , and three FGDs CaSO_4 , and three FGDs.^a

Treatment	Level in soil %	Zinc concentration (mg kg^{-1} DM)						Copper concentration (mg kg^{-1} DM)					
		ALF	WC	OGR	TF	SWG	EGG	ALF	WC	ORG	TF	SWG	EGG
Control	0	212	273	84	86	40	56	61.5	195.6	51.2	17.2	48.8	85.2
CaCO_3	0.125	85	64	58	41	38	50	36.2	20.0	28.8	18.9	35.1	54.9
	0.25	65	47	41	35	27	67	35.8	21.3	29.2	21.0	22.8	46.4
	0.5	40	32	32	28	21	57	24.4	13.4	19.7	17.5	13.6	58.1
CaSO_3	0.25	108	116	118	51	60	48	0.4	11.1	84.9	11.6	73.1	149.1
	0.5	116	146	95	62	71	88	0.1	10.0	63.2	36.6	80.6	91.6
	1.0	94	D	86	55	66	47	—	D	31.2	30.5	67.8	97.3
	2.0	D	D	91	52	44	D	D	D	28.3	23.9	21.0	D
	3.0	D	D	81	47	31	D	D	D	35.7	27.2	15.1	D
CaSO_4	5	138	136	145	115	38	—	10.9	15.0	151.0	17.4	34.4	—
	10	137	84	131	99	31	—	2.5	7.8	129.4	12.0	23.7	—
	25	120	121	155	101	24	—	0.8	53.1	103.4	17.8	15.3	—
	50	112	122	—	109	22	35	12.2	40.8	—	22.7	16.3	—
	75	81	89	144	61	23	55	4.3	23.8	87.0	13.1	19.0	68.9
FGD-22	5	76	120	76	45	22	70	30.7	21.4	31.8	24.7	17.7	123.3
	10	47	66	56	34	16	31	16.8	20.9	35.5	30.3	12.8	57.7



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FGD-27	25	18	28	40	27	8	38	13.4	13.8	39.5	20.1	6.4	43.0
	50	14	26	62	28	14	24	11.9	15.9	53.9	34.6	19.6	45.9
	75	20	30	89	50	32	17	12.9	11.4	67.4	39.2	53.3	9.1
	1.0	75	112	82	31	25	42	11.0	30.5	38.6	37.7	21.2	52.1
	2.5	78	107	61	43	21	46	9.9	18.7	47.5	34.9	20.0	66.4
	5.0	56	69	50	34	24	90	17.1	21.1	40.8	29.4	22.8	91.6
FGD-28	10	33	44	52	27	31	56	12.5	23.9	38.6	30.9	29.6	52.6
	25	15	42	47	24	20	31	6.8	7.6	38.9	32.2	12.9	5.4
	0.25	119	110	63	46	29	43	9.3	35.9	31.7	33.6	21.7	66.8
	0.5	83	95	99	53	24	38	7.5	21.8	44.4	30.8	16.6	60.6
	1.0	83	104	65	57	19	37	5.6	27.3	36.0	28.1	9.5	55.4
	2.0	85	110	61	40	21	44	12.7	25.1	29.8	32.2	21.7	46.8
LSD (P < 0.05)	3.0	87	90	58	45	20	61	55.6	27.1	44.0	34.7	21.1	73.0
		5	12	6	4	8	13	4.1	13.2	8.0	1.4	13.8	14.5
	Defic. conc. ^b	10	12	20	10 ^c	10 ^c	10 ^c	4	4	3	3–5 ^c	3–5 ^c	3–5 ^c
	High/toxic conc. ^b	100	25	50	50 ^c	50 ^c	50 ^c	50	10	10	25 ^c	25 ^c	25 ^c

D = dead plants.

^a Plant species were alfalfa (ALF), white clover (WC), orchardgrass (ORG), tall fescue (TF), switchgrass (SWG), eastern gamagrass (EGG).

^b Deficiency (defic.) and high/toxic concentrations (conc.) were taken from Smith^[30] and Jones et al.^[31]

^c Values are for an assortment of forage grasses.

Table 7. Shoot Mn and Fe concentrations of six forage species grown in acidic soil amended with various level of CaCO_3 , CaSO_3 , CaSO_4 , and three FGDs.^a

Treatment	Level in soil %	Manganese concentration (mg kg^{-1} DM)						Iron concentration (mg kg^{-1} DM)					
		ALF	WC	ORG	TF	SWG	EGG	ALF	WC	ORG	TF	SWG	EGG
Control	0	1946	1131	669	669	590	268	3422	344	542	1107	130	240
CaCO_3	0.125	242	243	462	362	256	94	158	509	246	145	85	195
	0.25	167	181	320	217	109	57	20	429	228	201	63	175
	0.5	192	148	283	182	134	81	51	299	818	141	73	198
CaSO_3	0.25	2380	1564	981	868	581	345	936	403	757	1685	137	356
	0.5	2086	1269	1115	1006	511	390	1131	276	874	1868	200	359
	1.0	1833	D	1334	959	478	432	2301	D	465	573	290	433
	2.0	D	D	1304	1110	425	D	D	D	397	247	459	D
	3.0	D	D	1702	1271	371	D	D	D	357	255	324	D
CaSO_4	5	1221	833	570	426	609	182	870	299	959	684	66	> 1000
	10	2683	599	634	883	679	284	590	179	536	842	77	> 1000
	25	1827	712	657	417	531	252	163	367	679	852	70	864
	50	1579	758	437	357	403	266	139	234	850	1210	64	469
	75	876	706	632	444	338	299	122	251	839	483	77	208
FGD-22	5	1340	764	725	724	533	148	185	398	209	456	83	326
	10	393	420	576	544	424	86	121	429	298	346	87	314



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FGD-27	25	149	190	362	299	124	89	191	323	590	323	74	127
	50	131	183	457	505	181	65	110	198	299	480	112	91
	75	103	142	554	782	178	64	96	191	347	384	93	107
	1.0	1266	1315	630	495	450	123	115	815	533	364	106	236
	2.5	905	843	582	559	360	118	110	668	377	266	79	260
	5.0	256	454	485	799	295	97	90	776	270	249	74	209
	10	187	225	491	358	239	104	48	451	226	190	74	205
FGD-28	25	118	204	350	132	154	101	74	511	198	190	108	142
	0.25	4122	1698	827	632	823	277	821	468	202	266	84	229
	0.5	3218	1850	894	691	864	281	871	437	692	461	78	190
	1.0	3292	1689	810	894	848	293	325	523	279	396	65	188
	2.0	2822	2126	829	779	854	200	287	700	235	291	78	168
	3.0	2399	1723	831	910	612	257	405	659	242	223	74	204
LSD ($P < 0.05$)		94	41	25	29	40	18	117	39	53	95	15	35
Defic. conc. ^b		20	20	50	25 ^c	25 ^c	25 ^c	30	45	50	25 ^c	25 ^c	25 ^c
High/toxic conc. ^b		250	600	150	700 ^c	700 ^c	700 ^c	400	100	200	250 ^c	250 ^c	250 ^c

D = dead plants.

^a Plant species were alfalfa (ALF), white clover (WC), orchardgrass (ORG), tall fescue (TF), switchgrass (SWG), eastern gamagrass (EGG).^b Deficiency (defic.) and high/toxic concentrations (conc.) were taken from Smith^[30] and Jones et al.^[31]^c Values are for an assortment of forage grasses.



Table 8. Shoot Al and Na concentrations of six forage species grown in acidic soil amended with various levels of CaCO₃, CaSO₃, CaSO₄, and three FGDs.^a

Treatment	Level in soil %	Aluminum concentration (mg kg ⁻¹ DM)						Sodium concentration (mg kg ⁻¹ DM)					
		ALF	WC	ORG	TF	SWG	EGG	ALF	WC	ORG	TF	SWG	EGG
Control	0	5912	525	508	1331	106	265	2747	684	498	601	78	132
CaCO ₃	0.125	230	528	210	155	44	151	220	235	326	115	76	93
	0.25	126	485	197	254	34	137	116	210	298	90	54	174
	0.5	138	305	237	144	46	71	104	229	315	104	69	208
CaSO ₃	0.25	2032	546	1335	2807	71	298	12290	5031	408	485	288	870
	0.5	2294	344	660	2658	87	230	26300	12320	366	358	876	1249
	1.0	4677	D	168	724	207	195	65580	D	390	279	4406	2646
	2.0	D	D	152	190	460	D	D	D	270	109	13110	D
	3.0	D	D	181	280	286	D	D	D	259	79	11640	D
CaSO ₄	5	1575	687	901	965	48	125	2104	430	491	660	66	14
	10	1422	370	1163	1470	46	68	582	268	485	716	101	18
	25	394	591	484	1443	38	374	354	310	470	775	88	14
	50	195	405	940	2544	39	171	319	298	403	1107	117	25
	75	159	254	939	900	28	347	311	365	355	474	124	245
FGD-22	5	310	317	190	208	52	294	202	564	278	102	95	282
	10	197	373	281	371	48	247	139	520	252	104	70	242



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FGD-27	25	284	368	369	239	18	60	182	443	344	153	60	439
	50	124	194	260	410	22	59	190	684	692	190	71	394
	75	75	159	363	366	24	62	212	795	732	267	86	377
	1.0	171	541	288	470	57	205	119	324	225	163	141	254
	2.5	33	421	420	327	54	178	173	258	245	120	147	269
	5.0	5	520	276	246	66	147	158	205	303	82	54	285
	10	3	495	189	234	49	133	160	147	368	125	62	358
FGD-28	25	16	539	177	252	27	69	169	395	796	142	182	385
	0.25	382	641	176	243	56	225	1177	285	276	145	20	204
	0.5	412	524	225	240	68	194	420	283	245	105	59	194
	1.0	143	443	190	254	39	197	404	310	210	118	20	181
	2.0	29	516	158	215	59	166	245	519	199	131	23	201
LSD (P < 0.05)	3.0	148	252	183	296	48	172	286	408	236	131	40	249
		274	43	94	163	17	31	605	30	25	39	260	46
High/toxic conc. ^b		100 ^c	100 ^c	200 ^c	200 ^c	200 ^c	200 ^c	NP	NP	NP	NP	NP	NP

D = dead plants.

^a Plant species were alfalfa (ALF), white clover (WC), orchardgrass (ORG), tall fescue (TF), switchgrass (SWG), eastern gamagrass (EGG).

^b High/toxic concentrations (conc.) were taken from Smith^[30] and Jones et al.^[31]

^c Values are for an assortment of forage grasses and legumes; NP = Not provided.

allow free flow of Na and possibly Al into roots for translocation to shoots. Aluminum concentrations decreased consistently in plants grown in soil where pH increased, namely for plants grown with CaCO_3 and FGD-27 (Table 8). Accumulation of Al in plants can be reduced extensively by increasing soil pH to inactivate Al.^[38] With exception of switchgrass for the most part, Al concentrations in plants were on the high side and could potentially be associated with detrimental effects on growth.

Concern for trace element contamination in plants arises whenever plants are grown in soils amended with coal combustion products (CCPs), including FGDs. Although somewhat variable for each plant species, shoot concentrations of Mo, Ni, Cd, Cr, and Pb were relatively low and within normal ranges reported for plant foliage (Table 9). The forage species did not acquire abnormally high concentrations of trace elements from this FGD amended acidic soil. Similar results for plant accumulation of Ni, Cd, Cr, and Pb were reported for maize grown in acidic soil amended with 15 CCPs, of which nine were FGDs.^[19] Of interest, shoot concentrations of these trace elements were sometimes higher in maize grown in unamended acidic soil (pH 4) than in soil amended with CCPs. Nevertheless, As and Se near or above

Table 9. Shoot trace element concentrations (mean \pm standard error) over all treatment levels and products/ substances for plants grown with various amendments in acidic soil.

Plant species ^a	Trace element concentration ($\text{mg Kg}^{-1} \text{ Dm}$)				
	Mo	Ni	Cd	Cr	Pb
White clover	1.10 ± 2.34	5.64 ± 6.54	1.59 ± 2.04	0.97 ± 0.47	0.56 ± 0.96
Orchardgrass	1.52 ± 2.68	2.30 ± 1.69	0.83 ± 0.38	0.75 ± 0.53	0.74 ± 0.82
Tall fescue	1.28 ± 2.25	1.05 ± 1.66	0.53 ± 0.45	1.07 ± 1.24	0.40 ± 1.02
Switchgrass	0.87 ± 0.95	1.89 ± 1.71	0.56 ± 0.38	1.34 ± 1.89	1.88 ± 1.95
Eastern gamagrass	1.03 ± 1.28	1.17 ± 0.60	0.85 ± 0.69	0.68 ± 0.41	1.25 ± 1.64
Overall	1.19 ± 1.96	2.45 ± 2.49	0.88 ± 0.78	1.00 ± 0.96	0.76 ± 1.30
Normal in foliage ^b	0.3–5	0.2–5	0.1–2.4	0.03–14	0.2–20
Critical total in foliage ^b	10–50	8–220	4–200	2–30	30–300

^a Data for alfalfa not included because of analytical instrument problems at the time.

^b Values taken from information provided by Alcordo and Rechcigl,^[1] Alloway,^[45] Bilski et al.,^[2] Kabata-Pendias and Pendias,^[46] MacNicol and Beckett,^[47] and Stout et al.^[48]



critical concentrations in plant tissue were reported for maize grown in soil with 8 and 10% levels of a FGD.^[25]

CONCLUSIONS

Results indicate that FGDs used in this study can be useful as amendments at appropriate levels to acidic soils without detrimental effects on the growth of legumes and grasses or animals that consumes them.

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